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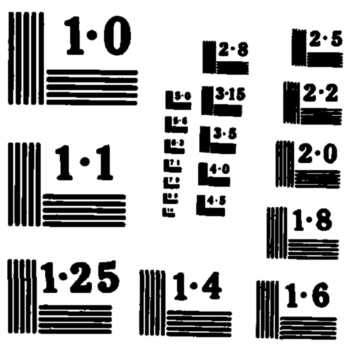
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August 14, 1985

Dr. K. J. Wynne
Head Chemistry Division (Code 413)
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

Re: First Annual Report for ONR Contract N00014-85-K-0161

Dear Dr. Wynne:

This

The following report details the progress made and work currently being undertaken on the project Condensation Polymers with Controlled Structure, for which funding began in February of 1985. ~~Growth has taken~~ place in areas of: polymer synthesis with controlled constitution, monomer preparation, polymer characterization and theoretical understanding of polymer properties. This report is organized as follows:

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1 Introduction

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The project's objective is to develop new rigid-rod polyamides with a controlled and preselectable degree of constitutional regularity. The reason behind this approach is the fact that condensation polymers that contain units whose mutual orientation can be distinguished give rise to constitutional isomerism similar to the "head/tail" isomerism in vinyl polymers. Regular polymers are characterized by structures containing either only "head-to-tail" or only "head-to-head/tail-to-tail" structures. This isomerism has been found to influence the properties of many polycondensates significantly.

At present, no molecular theory of the properties of condensation polymers exists and the mechanisms by which properties differ are largely unknown, but one might conjecture that crystallinity and intermolecular cohesion are both important factors. Both types of regular structures should be able to merge into crystalline domains and form more hydrogen bonds, etc.; the more random structures should have difficulty to crystallize and be "less cohesive."

To take full advantage of the potential inherent in the dependence of properties on structure, we have selected a polymer system that depends largely upon inter-chain interactions. Rigid-rod polymers are such systems and the one which we have selected to begin our study on are substituted wholly aromatic polyamides or, as they are often referred to as, aramides. The aramide chains are highly extended and have limited flexibility. Thus, when dissolved, they form anisotropic phases (liquid crystalline domains) in which the macromolecules are aligned relative to each other with a high degree of order. This spontaneous development of order seems to be responsible for the very high crystallinity and orientation order of the fibers formed from the anisotropic solutions and seems to be a major cause for their excellent thermal and mechanical properties. However, aramides that have been commercialized to date (i.e. those where constitutional isomerism is either not possible or not controlled) are soluble only in noxious solvents and melt at unpractical high temperature making processing unusually difficult.

We have begun to prepare modified aramides from non-symmetric monomers. We expect to be able to control crystallinity which we believe to be the main cause of their undesirable properties without affecting their rigid-rod character which is the main cause of their desirable properties. The following section deals with the first two polymers prepared in this series.

2 Polymers Synthesized

We have synthesized two modified aramides thus far: Poly(2-dimethyl-p-phenyleneterephthalamide), I, and poly(2,6-dimethyl-p-phenyleneterephthalamide), II. The constitutional order of these polymers was influenced by empirical variations in the monomer feed rates and solubilities were shown to be affected by the order.

2.1 Synthetic Techniques

A number of novel synthetic procedures were employed to prepare our polymers. The above polymers were both synthesized with degrees of polymerization (X_n) greater than twenty. In all methods the basic reaction is nucleophilic attack by the amino group of the non-symmetric diamine (XabX) upon the carbonyl group of the symmetric diacid chloride (YccY). The procedure which proved most satisfactory was the Schotten-Baumann solution method. The acid halide and the non-symmetrical diamine are separately dissolved in nearly identical solvent systems and then added to one another in a predetermined manner according to the constitution desired. In both of our polymers the solvent system consisted of hexamethlphosphortriamide (HMPT) and N-methyl-pyrolidone (NMP) with HMPT:NMP=2:1 (this ratio provides a good environment for amidation and for dissolution of the polymer).

Chain constitution was inferred from proton nuclear resonance spectroscopy. Quantitative measurements have proved impossible thus far but qualitative differences in order were obtainable. Better nmr techniques are currently being investigated in order to obtain accurate quantitative information on constitution (see Section 4.3 below). For example, more powerful ^{1}H, ^{13}C and ^{15}N nmr.

In all, five different "constitutionally controlled" aramides with 2-methyl or 2,6-dimethyl moieties on the p-phenylenediamine ring were synthesized. As already stated, constitution was influenced by empirical variations in the feed rates. Order is depicted by the parameter s, such that:

s = 0 denotes an ordered constitution (head-to-head/tail-to-tail)

s = 1/2 denotes a random constitution

s = 1 denotes an ordered constitution (head-to-tail).

The parameter Q describes the manner in which one monomer is added to another. In these cases:

Q = 1, XabX is added "infinitely" slowly to YccY;

Q = 0, XabX and YccY are immediately mixed; and

Q = -1, YccY is added "infinitely" slowly to XabX

Table 2-1 summarizes the results of the syntheses of these five polymers.

TABLE 2-1: "Random" and "Ordered" Polymers Synthesized and Properties

Polymer[a]	Process	η_{inh}[b] (dl/g)	Solubility[c] DMSO/LiCl (mg/ml)	DMF/LiCl
P1	Q ≈ 1	0.20	66	-
P2	Q ≈ -1	0.18	21	-
P3	Q ≈ 0	0.20	50	10
P4	Q ≈ 1	0.32	41	10
P5	Q ≈ -1	0.27	22	10
Kevlar™		0.15	10	-

[a] P1: Poly(2-methly-p-phenyleneterephthalamide) s ≈ 1/2
P2: " s → 0
P3: Poly(2,6-dimethly-p-phenyleneterephthalamide) s → 1/2
P4: " s ≈ 1/2
P5: " s → 0

[b] At 30°C, in H_2SO_4 (96%w/w), 0.5 g/dl.

[c] Maximum amount of polymer that results in an apparently homogeneous solution.

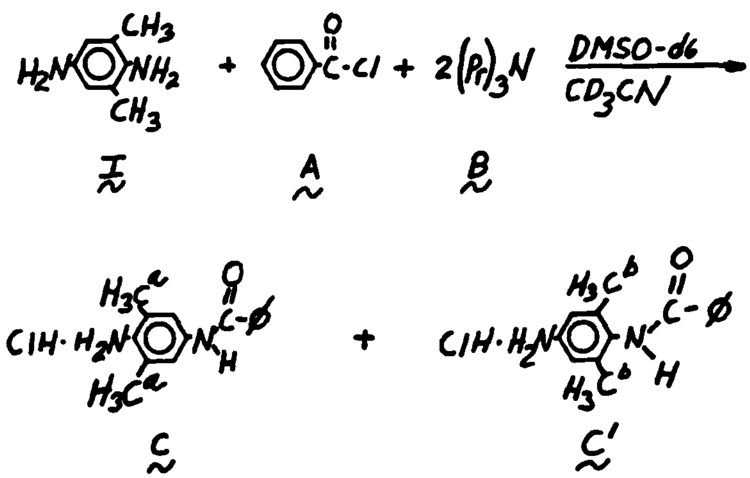
2.2 Properties of Polymers with Controlled Constitution

Solubility and thermal analyses were performed on all polymers synthesized. All DSC runs showed thermal stabilities nearly identical to that of an unsubstituted aramide (Kevlar™) synthesized by the Schotten-Baumann interfacial technique. Thus, the excellent thermal stability of Kevlar™ was retained by the substituted polymers. Degradation was observed in all cases with no detectible conventional melt temperature. Future studies on these and other polymers will include thermogravimetric analysis (TGA) in order to quantify the degradation of these polymers.

Table 2-1 also contains the results of the solubility studies performed on all polymers. All substituted polymers are more soluble than Kevlar™. In addition to this, "random" methyl substituted aramides showed greater solubility than "regular" (head-to-head/tail-to-tail) ones. This result agrees with expectations (see Section 1).

2.3 Measurement of the Relative Amino Group Reactivities

Reactivity ratios are determined by performing a competitive reaction between a monofunctional aromatic acid chloride, benzoic chloride, and the non-symmetric monomer, after rapid mixing. The quantitative ratio of the products reflects the kinetic reactivity ratio, r, of the functional groups. Care must be taken to avoid any side reactions and an acid scavenger must be present to avoid effects of increasing acidity of the reaction medium with extent of reaction as well as to represent polymerization conditions. The product mixture is quantified using ^{1}H nmr spectroscopy. The following reaction scheme is used in the r determination for the 2,6-dimethyl-p-phenylenediamine monomer.



For this monomer, methyl resonances for a (unreacted) and b (reacted) sides were identified at 2.04 and 2.06 ppm respectively. There is some peak overlap which yields uncertainty in the peak area determination used to quantify the value of r. Nonetheless the C/C' product ratio (equal to r) was determined to be 0.19. This value confirms what had already been suspected from the relatively small differences in properties between the polymers of different order: r is to close to unity to achieve constitutional control over the entire range of s.

2.4 Conclusions

The conclusions that can be drawn from our polymer syntheses and the parallel determination of the reactivity ratios thus far performed are:

(1) We can synthesize substituted aramides to high degrees of polymerization.

(2) These substituted aramides are much more soluble than Kevlar™ in two different organic solvents.

(3) These substituted aramides retain very good thermal stability, up to 450 C in N_2, but do not melt in the absence of decomposition.

(4) The chain constitution of our polymers is influenced by empirical variations in the monomer feed rates. Due to the reactivity ratios of these methyl substituted monomers being too close to unity, we will not be able to achieve constitutional control over the entire range of s.

(5) Nevertheless, the "random" polymers were more soluble in two different solvents than the "ordered" polymers.

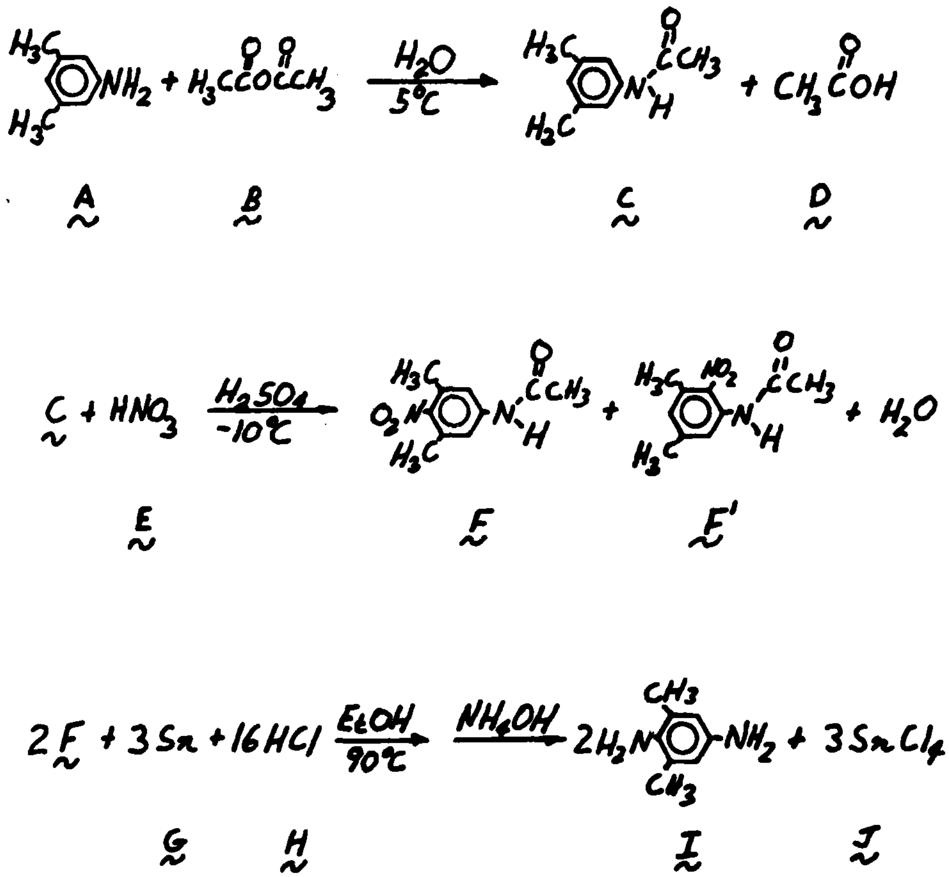
Due to the dependence of s on the monomer reactivity ratio we have decided to move on to monomers with lower reactivity ratios. Two new monomers have been investigated with reactivity ratios of order 10^{-2}.

3 Preparation of More Promising Monomers

As mentioned in Section 2.3, the amino groups in 2,6-dimethyl-p-phenylenediamine and 2-dimethyl-p-phenylenediamine are not of sufficiently different reactivity to allow the preparation of highly constitutionally ordered chains. Hence, new (and more promising) monomers have been prepared and purified to be used with modified polymerization techniques. Again the symmetric monomer was terephthaloyldichloride. The two most promising non-symmetric monomers are 2,6-dichloro-p-phenylenediamine and 2,6-dimethoxy-p-phenylenediamine. The chloro and methoxy moieties were selected because they are strong electron acceptors and provide large steric hinderance of an ortho-amino function and thus tend to decrease the rate of amidation at the neighboring amino group.

3.1 Synthetic Techniques

The 2,6-dichloro-p-phenylenediamine monomer can be purchased with 97% purity from Polysciences Incorporated. To achieve the 99.9% purity required for structurally controlled polymerizations, the monomer is sublimed in vacuo no less than two times. The 2,6-dimethoxy-p-phenylenediamine monomer must be synthesized. Synthesis of this momomer is not a trivial affair for yields are very low. The following synthetic scheme has proved to be the best thus far:



After separation, this monomer is also purified by double vacuum sublimation.

3.2 Determinations of Reactivity Ratios

Reactivity ratios are determined as described in Section 2.3. Preliminary studies indicate that the reactivity ratio of the dichloro monomer is on the order of 0.01 to 0.1. More work is required to further quantify this result.

4 Polymer Characterization

The characterization of rigid-rod structures, and hence of aramides, is not easy. Rigid-rod structures are not sufficiently soluble in ordinary organic solvents for many routine methods and this provides a stumbling block in molecular level characterization. In addition, the chain rigidity creates new special problems in many techniques.

4.1 General Rigid-Rod Behavior

Linear flexible polymer chains are viewed as forming random coils in solutions, whereas extended-chain aromatic polyamides are more nearly comparable in behavior to rigid-rods which can exist in a random array only in dilute solution. With increasing polymer concentration, the polymer chains and combined solvent associate in parallel alignment in regions or domains. The ordered regions constitute a liquid crystalline state and exist as a separate phase in the initially continuous isotropic phase. Continued addition and dissolution of the polymer forces more polymer into the order state until only an anisotropic phase exists. This phase is referred to as the nematic phase and is very common in solutions of para-linked aramides.

Due to the liquid crystalline behavior of these polymers many of the standard molecular level polymer characterization techniques are fraught with complications. Hence, we have begun to develop techniques that will make these polymers more flexible <u>without</u> interfering with their order or degree of polymerization.

4.2 Trifluoroacetylation and New Solvent Systems

Using trifluoroacetylation and novel synthetic techniques has comprised our most recent efforts in the area of characterization. The well documented technique of trifluoroacetylation replaces the sole amide hydrogen with $-COF_3$. This makes the <u>cis</u> conformation of the amide group frequent (non-N-substituted amides strongly prefer the <u>trans</u> configuration) and allows the chain to assume a more random coiling configuration. Thus, the polymers should dissolve in the same common organic solvents that dissolve ordinary aliphatic polyamides (nylons) and should be characterized without great difficulty. Thus far, the technique has not been successful on aramides; we feel that this lower reactivity of the aromatic amide hydrogen as compared to its aliphatic counterpart can be overcome. Work in this area is continuing.

New solvents and solvent systems are also being used to dissolve our polymers. We have recently acquired an experimental solvent from DuPont de Nemours Inc., tetramethylmethylphosphor-

amide, which promises to cause increased solubility as well as more rapid polymerizations.

4.4 Instrumental Methods

To date only ^{1}H nmr and dilute solution viscometry (in 98% sulfuric acid) have been used to determine molecular level characteristics. Work has begun on determining the feasibility of the following techniques:

(1) Size Exclusion Chromatography
(2) Light Scattering
(3) ^{13}C and ^{15}N nmr
(4) Solid State nmr

5 Concluding Remarks

The first steps have been taken in this project. We have learned a great deal about these substances and are convinced that we will be able to control polymer constitution throughout the entire range of order. These preliminary findings have also revealed that order effects properties in aramides and thus opens the door for a wide spectrum of exciting possibilities.

We are grateful to the Office of Naval Research for providing the opportunity to conduct this research.

Sincerely,

Ulrich W. Suter

Ulrich W. Suter
Texaco-Mangelsdorf
Associate Professor

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